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United States Patent
Kamen , et al.

6,093,455
July 25, 2000

Method and compositions for *decorating glass*

Abstract

A method for *decorating* a vitreous article, in particular, a *glass* substrate, comprising applying to the *glass* in a predetermined design a radiation curable *ink* composition which is (i) operable when cured to bond to *glass*, and (ii) *strippable from the glass* upon exposure to alkali, and curing the *ink on the glass* by exposing it to the radiation by which it is curable, thereby bonding the *ink to the glass*; and related compositions; as well as a method for stripping the decorative indicia from *glass* upon exposure to alkali, and the related compositions.

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 106/31.05,31.32,31.64

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This application is a continuation-in-part of U.S. patent application Ser. No. 08/862,304, filed May 23, 1997, entitled "Method and Compositions For *Decorating Glass*", by inventors Melvin Edwin Kamen, and Ming Hu, now abandoned.

We claim:

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aqueous alkaline solution at a temperature of about 60 to 100.degree. C.

23. The method of claim 21 wherein the radiation cured **ink** composition is a polymeric composition formed by the polymerization of ethylenically unsaturated monomers or oligomers having at least one free acid group.

24. The method of claim 23 wherein the ethylenically unsaturated monomers or oligomers are acrylates or methacrylates.

25. The method of claim 23 wherein the acid group is a carboxylic acid group, a sulfonic acid group, or a phosphoric acid group.

26. The method of claim 25 wherein the acid group is a carboxylic acid group.

Description

TECHNICAL FIELD

The invention is in the field of **decorating** vitreous articles with radiation curable inks. In particular, the invention relates to decoration of vitreous articles such as **glass**, with radiation curable inks which, to facilitate recycling, are capable of being chemically removed from the **glass** upon exposure to alkali for a specified period of time.

BACKGROUND OF THE INVENTION

Commercial ceramic and glassware is often decorated by applying a pattern in colored **ink** on the surface of the substrate with screen printing, offset printing, or any other direct application technique. The **glass** is then baked at high temperatures to bond the design or indicia to the **glass** surface. This process, sometimes referred to as applied ceramic labeling (ACL), exhibits certain drawbacks. Often, the **ink** compositions contain heavy metals and volatile organic solvents (VOC's). Both VOC's and heavy metals are undesirable from the environmental point of view. Second, ACL requires high temperature ovens for the baking step, which results in considerable energy usage and an increased potential for worker injury due to the high temperatures at which the process operates. Moreover, the high temperature ovens are expensive, cumbersome pieces of equipment which require considerable floor space in factories.

The decoration of **glass** with ultraviolet (UV) radiation curable organic pigmented inks for the decoration of **glass** and ceramic ware is known in the art. Organic inks generally can be cured by exposure to radiation, such as ultraviolet radiation, thus obviating the need for high temperature baking. In addition, UV curable organic inks can be formulated to contain little or no VOC's or other nonaqueous solvents. Organic inks generally exhibit excellent adherence to **glass**.

In many countries, it is mandatory that beverages such as beer and soda, be marketed in returnable **glass** bottles. After the beverage has been consumed, the **glass** bottles are returned to the beverage filler. They are then cleaned, sterilized, refilled, relabeled, then sold again. Decals and paper labels are most often used to decorate returnable beverage bottles. Both types of labels have many drawbacks. For example, both paper labels and decals are expensive. In addition, they are messy, and can easily come off upon exposure to water or other materials. In addition, many of the adhesives used in decals become sticky when subjected to the bottle cleaning process, and cause machines, drains, etc. to be gummed up.

There is a need for a method to decorate returnable beverage bottles that provides excellent decorative effect. In addition, the method must be cost competitive when compared to paper labels and decals. At the same time the decorative indicia applied should be easily **strippable from the glass** container between fillings.

SUMMARY OF THE INVENTION

The invention is directed to a method for **decorating** a vitreous article comprising the steps of:

a) applying to the vitreous article in a predetermined design a radiation curable **ink** composition which is (i) operable when cured to bond to the vitreous article, and (ii) **strippable** from the vitreous article upon exposure to alkali,

b) curing the *ink* on the vitreous article by exposing it to the radiation by which it is curable, thereby bonding the *ink* to the vitreous article.

The invention is also directed to a method for stripping decorative indicia from a vitreous article decorated with a radiation cured *ink* composition containing free acid groups which is (i) operable, when cured, to bond to the vitreous article, and (ii) *strippable* from the vitreous article upon exposure to alkali, comprising contacting the vitreous article with an aqueous alkaline solution containing 2-20% by weight alkali for a period of approximately 1 to 120 minutes.

The invention is directed to a *ink* composition comprising, by weight of the total composition:

5-95% of an acid functional monomer or oligomer,

5-95% of a monomer or oligomer that does not contain free acid groups,

5-95% pigment.

DETAILED DESCRIPTION

All percentages mentioned herein are percentages by weight unless otherwise indicated.

The radiation curable *ink* compositions used in the method of the invention must be operable, when cured, to bond to the vitreous article, which is preferably *glass*. In particular, the *ink* compositions must be capable of adhering to *glass* to a degree sufficient to permit use as a commercial container used for beverages or other consumable materials. At the same time, the polymerized *ink* compositions must be capable of being readily stripped or removed from the *glass* upon exposure of the decorated *glass* to alkali. *Glass* containers are filled; then they are decorated with the radiation curable *ink* compositions. After the beverage in the container is consumed, the container is returned to the filler. The decorative indicia is stripped from the *glass* upon exposure to alkali. The containers are then cleaned, sterilized, re-filled, re-decorated, and shipped again.

Generally, **strippable ink** compositions are made from radiation curable monomers and/or oligomers having at least one free acid group. The term "free acid" means an acidic group which is capable of reacting with alkali. Examples of such acidic groups are carboxylic acid groups, phosphoric acid groups, sulfonic acid groups and the like. Preferably, the acid group is a carboxylic acid group. The resulting polymerized coating contains free acidic groups which, upon exposure to alkali, react with the alkali to form a salt. As a result, the decorative indicia are much more readily removable from the **glass**. It should be noted that in order for radiation cured **glass** coatings to be considered "high performance", decorative indicia must be capable of withstanding exposure to a concentrated aqueous alkali solution for a period of two to four hours. In contrast, the radiation cured **ink** compositions of the invention must be completely removed from the **glass** container upon exposure to aqueous alkali before two hours has lapsed; after a period of about 1 to 120 minutes, preferably about 1 to 60 minutes, more preferably about 5 to 30 minutes.

THE *INK* COMPOSITIONS

The Acid-Functional Monomer and/or Oligomer

The **ink** compositions used in the method of the invention, contain about 5-95%, preferably about 10-85%, more preferably about 15-75% of a monomer, oligomer, or low molecular weight homo- or copolymer having at least one free acid group. A variety of such materials are suitable, provided they have at least one free acid group, such as a carboxylic acid, sulfonic acid, or phosphoric acid group. The phrase "having at least one free acid group" means that the monomer unit has at least one free acid group, or the oligomer contains at least one monomer unit containing a free acid group, or if a homo- or copolymer, at least one monomer unit thereof contains at least one free acid group. Preferably the **ink** composition contains a monomer or oligomer, in particular an ethylenically unsaturated monomer or

Preferably the monomer or oligomer is of Formula II wherein R.sub.1 is H or CH.sub.3, and R.sub.2 is X--COOH wherein X is a C.sub.1-10 straight or branched chain alkyl, more preferably ethyl. More preferably R.sub.2 is beta-carboxyethyl, e.g. as in beta-carboxyethyl acrylate, which is sold under the tradename B-CEA by UCB Radcure, Inc. B-CEA is a reactive monomer which contains both acrylate and carboxylic acid functionality, predominantly as the acrylic acid dimer, and, in particular, is a mixture of about 40% by weight B-carboxyethylacrylate, about 40% by weight higher homologs of acrylic acid, and about 20% by weight of acrylic acid. The B-carboxyethylacrylate component of this mixture has the following formula: ##STR3##

Particularly preferred aromatic partial esters of anhydride containing copolymers are those sold by Sartomer, Inc. under the SARBOX.RTM. tradename, such as SB-400, SB-500, and SB-600. Particularly preferred is aromatic acid methacrylate half ester in ethoxylated trimethylolpropane triacrylate, which is sold by Sartomer, Inc. under the tradename Sarbox SB500E50.

Examples of monomers containing sulfonic acid groups include 2-acrylamido-2-methyl-1-propanesulfonic acid; 2-methyl-2-propene-1-sulfonic acid, 2-propene-1-sulfonic acid, 4-styrenesulfonic acid, 2-sulfoethyl methacrylate, 3-sulfopropyl dimethyl-3-methacrylamidopropyl ammonium inner salt, 3-sulfopropyl methacrylate, vinylsulfonic acid, and so on.

Additional Polymerizable Reactants

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or copolymers, terpolymers, graft copolymers of the above monomers provided they have a molecular weight of less than about 50,000, otherwise it is too difficult to effect polymerization, i.e. curing. Preferred are acrylate homopolymers or acrylate or methacrylate copolymers, preferably acrylate or methacrylate copolymers. Examples of such acrylate or methacrylate copolymers include epoxy acrylates, copolymers of propylene glycol and a dicarboxylic acid, urethane acrylates, and the like. Preferably, the compositions contain one or more polymerizable reactants selected from the group consisting of urethane acrylate copolymers, tripropylene glycol acrylate, epoxy acrylate, and mixtures thereof.

Preferably, the radiation curable compositions of the invention contain about 5-95% by weight of acrylate or methacrylate monomers, or homo- or copolymers which do not contain acid functional groups.

Pigment

The compositions used in the invention preferably contain 5-95%, preferably 5-50%, more preferably 8-35% by weight of the total composition of pigment. A wide variety of pigments are suitable including organic and inorganic pigments. Examples of such pigments are set forth in U.S. Pat. No. 5,178,952, which is hereby incorporated by reference. Inorganic pigments include extender pigments such as barytes, barium sulfate, calcium carbonate, talc, clay, alumina, titanium dioxide, white carbon, chinese white, zinc sulfide, lithopone, ultramarine, Prussian blue, cobalt, chrome oxide, viridian chrome green yellows, oranges, and reds, cadmium, chromium, iron oxides, carbon black, metallic pigments, aluminum powder, bronze powder, zinc chromate, strontium chromate, zinc dust, copper, and so on. Examples of suitable organic pigments include azo

pigments, indolinones, isoindolinones, vat pigments, the Lakes, phthalocyanine pigments and so on. The preferred pigment to impart white color to the *ink* composition is titanium dioxide. Preferred red and yellow pigments are isoindolinones and pyrrolopyrrols as disclosed in U.S. Pat. Nos. 4,415,685; 4,579,949; 4,791,204; 4,666,455; 5,074,918; 4,783,540; 4,914,211; 4,585,878; as well as U.S. Pat. No. 5,571,359 of Kamen, et. al., all of which are hereby incorporated by reference. These pyrrolopyrrols are generally of the formula: ##STR5## wherein R.sub.1 and R.sub.2 are each independently alkyl, arylalkyl, aryl, substituted or unsubstituted isocyclic or heterocyclic aromatic radicals; R.sub.3 and R.sub.4 are each independently H, substituted or unsubstituted alkyl, alkoxycarbonyl, aroyl (e.g. benzoyl), arylalkyl (e.g. benzyl), aryl (e.g. phenyl), alkanoyl, C.sub.5-6 cycloalkyl, alkenyl, alkynyl, carbamoyl, alkylcarbamoyl, arylcarbamoyl, or alkoxycarbonyl; and X is O or S. Preferred is a compound wherein R.sub.1 and R.sub.2 are each independently phenyl or naphthyl, R.sub.3 and R.sub.4 are hydrogen, and X is O. Particularly preferred as a red pigment is pyrrolo 3,4-C pyrrol-1,4-dione, 2,5-dihydro-3,6-di-4-chlorophenyl which has a CAS number 84632-65-5 and is known by the common name C.I. pigment red 254. This pigment is commercially available from Ciba-Geigy Pigments Division, Newport, Del., under the tradename Irgazin DPP Red 80. Other Ciba-Geigy red pigments sold under the tradename Irgazin are also suitable.

Suitable isoindolinones are as set forth in U.S. Pat. Nos. 3,884,955, 3,867,404, 4,978,768, 4,400,507, 3,897,439 and 4,262,120 and 5,194,088 all of which are hereby incorporated by reference. Preferred isoindolinones are tetrachlorocyanobenzoic acid alkyl esters, particularly benzoic acid, 2,3,4,5-tetrachloro-6-cyano-methyl ester which is reacted with 2-methyl-1,3-benzenediamine and sodium methoxide. This pigment composition has the common name C.I. Pigment Yellow 109 and is available commercially from Ciba-Geigy Pigments Division, NewportDel. under the tradename Irgazin yellow 2GLTE. Other pigments in the Irgazin Yellow series as manufactured by Ciba-Geigy are also suitable.

Particularly suitable are blue pigments marketed by Ciba-Geigy under the tradename Irgazin Blue X-3367, or by Whittaker, Clark, & Daniels under the tradename Ultramarine Blue 5009.

Defoaming Agent

The *ink* compositions used in the invention also preferably contain about 0.01-10% of a defoaming agent, preferably a polyether-containing defoaming agent, which will cause the *ink* to apply smoothly on the *glass* substrate without bubbles or unevenness. A wide variety of defoamers are suitable, but preferred are defoamers sold by BYK Chemie under the BYK tradename. Examples of such defoaming agents are alkylvinyl ether polymers set forth in U.S. Pat. No.

5,187,201, which is hereby incorporated by reference. Examples of other defoamers include polyethers such as BYK-052, BYK-053, and BYK-033. BYK-052 and -053 are polyethers such as polyethylene or polypropylene glycol ethers, and in particular, polyvinyl ethers. Also suitable is BYK-354 which is a polyacrylate solution, and BYK-022 which is a mixture of hydrophobic solids and foam destroying polysiloxanes in polyglycol. Preferably the polyether defoaming agent is an alkoxyated alkyl phenol, more particularly a mixtures of petroleum distillates and an ethoxyated alkyl phenol, such as that sold by BYK-Chemie under the tradename BYK-033.

Adhesion Promoter

The **ink** compositions used in the invention also preferably contain about 0.01-25%, preferably about 0.05-15%, more preferably about 0.1-5% of a silane adhesion promoter which will enhance adhesion of the cured resin to the **glass** surface. Examples of silanes are silane esters, vinyl silanes, methacryloxy silanes, epoxy silanes, sulfur silanes, amino silanes, or isocyanato silanes. Suitable silanes include organofunctional silanes of the formula: ##STR6## wherein n=0-3 a=0-2 ##STR7## X is each independently CH₃, Cl, OCOCH₃, OC(H)₄OCH₃, (OC(H)₄)₂OCH₃, or --OR, where R is a C₁₋₂₀ straight or branched chain alkyl, preferably methyl or ethyl.

Silanes having this formula are commercially available under the Dynasytan trademark from Huls, America, Inc., Piscataway, N.J. or Osi Specialities Inc. Other organofunctional silanes such as those disclosed in U.S. Pat. No. 5,221,560, which is hereby incorporated by reference, are also suitable. Such organosilanes are acryloxyfunctional silanes including 3-methacryloxypropyltrimethoxysilane, 3-acryloxypropyltrimethoxysilane, 2-methacryloxyethyltrimethoxysilane, 2-acryloxyethyltrimethoxysilane, 3-methacryloxypropyltriethoxysilane, 3-acryloxypropyltriethoxysilane, 2-methacryloxyethyltriethoxysilane, 2-methacryloxyethyltriethoxysilane, 2-acryloxyethyltriethoxysilane, etc. Suitable glycidoxy silanes include 3-glycidoxypropyltrimethoxysilane, 2-glycidoxyethyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, 2-glycidoxyethyltriethoxysilane, 3-glycidoxypropyltrimethyl silane, and so on. Preferred for use in the compositions of the invention are acryloxy- functional silanes, isocyanato silanes, and amino silanes. The preferred acryloxy- functional silane is 3-methacryloxypropyl trimethoxy silane, which is sold by Huls America, Inc. under the tradename DYNASYLAN MEMO. The preferred amino silane is sold by Huls America, Inc. under the tradename DYNASYLAN TRIAMO. The preferred isocyanato silane is sold by Osi Specialities Inc., under the tradename A-1310. In the preferred *ink* compositions of the invention a mixture of the three silanes is preferred, generally 0.01-2% by weight of each.

Surfactant

The **ink** compositions also preferably contain 0.01-20%, preferably 0.5-10%, more preferably 1-5% by weight of a fluorinated surfactant. The term "fluorinated surfactant" means a fluorine containing compound having at least one lipophilic group or portion and at least one hydrophilic group or portion. In particular, fluorocarbon or fluorosilicone surfactants are most desirable. Suitable surfactants include those set forth in U.S. Pat. No. 4,961,976 which is hereby incorporated by reference. Preferred are fluorocarbon surfactants, such as those marketed under the Fluorad trademark by 3M Company. These fluorochemical surfactants include fluorinated alkyl esters, fluorinated alkyl polyoxyethylene ethanols, and the like. Particularly preferred are nonionic fluorinated alkyl alkoxylates e.g. those marketed by 3M under the trademark FC-171. Preferred are fluorinated C₈-30 alkyl ethoxylates and propoxylates.

Photoinitiator

The **ink** compositions preferably contain a photoinitiator which catalyzes the polymerization of the monomers upon exposure to the radiation by which the monomers are curable. There are generally two types of photoinitiators: free radical and cationic. Free radical initiators are more commonly used with ethylenically unsaturated monomers and oligomers, while cationic photoinitiators are used with epoxy or vinyl ether functional resins. Preferably, the compositions used in the invention contain free radical photoinitiators. Suitable free radical-type photoinitiators include carbonyl compounds such as ketones, acetophenones, benzophenones, and derivatives thereof. Examples of such materials include, for example, methyl ethyl ketone; benzophenone; benzyl dimethyl ketal; 1-hydroxycyclohexylphenylketone; diethoxyacetophenone; 2-methyl-1-(methylethiophenyl)-2-(4-morpholinyl)-1-

The **ink** composition is applied to the article to be decorated in a predetermined design using a variety of printing methods including screen printing, offset printing, gravure, hand painting and the like. After the **ink** is applied the substrate or article is irradiated with UV or actinic radiation using a conventional UV light source. The term "UV" means ultraviolet light which generally has a wavelength of 4 to 400, preferably 325 to 400 nanometers. The term "actinic" means radiation having a wavelength of 200 to 600 nanometers. Electron beam may be used instead of a UV light source. If a UV conveyer is used, it is set up so that the substrate passes through the beam of radiation for an amount of time appropriate to completely cure the **ink** composition and cause it to adhere to the substrate. If desired, the substrate may be moved through the conveyer in one or more passes to achieve the required curing. The appropriate time varies depending on the **ink** formula, but generally curing is complete in a period of time ranging from fractions of a second to 30 minutes. It is preferred, that by the time the decorated substrate or article is removed from the conveyer, the **ink** is completely cured and fused to the substrate surface. In some cases it may be necessary to subject the newly screened **glass** container to slightly elevated temperature prior to UV curing the applied **ink** on the substrate, or to an additional post-UV cure application of heat to finally polymerize the **ink** on the substrate. Preferably, the decorated substrate is subjected to post-UV cure heating at a temperature of 90 to 200.degree. C., preferably 100-200.degree. C. for a period of 0.5 to 30 minutes.

The **ink** compositions are well suited for use in automated systems such as the multiple color printing apparatus disclosed in copending application Ser. No. 432,485, filed May 1, 1995 by Kamen, et al., entitled "Apparatus and Method For Screen Printing Radiation Curable Compositions", or with the methods disclosed in U.S. Pat. No. 5,562,951, both of which are hereby incorporated by reference.

In another embodiment of the invention, it is possible to make the *ink* composition of the invention without the pigment and print it on the *glass* substrate in predetermined design according to the methods described above. For example, a substrate such as a container may be decorated in a pre-determined design by silk screening the unpigmented *ink* composition on the substrate and curing with the appropriate radiation. A layer of hot stamping foil is then compressed against the substrate with a press which is heated to a temperature sufficient to cause the hot stamping foil to adhere to the printed *ink* design but not to the *ink*-free areas of the *glass*. Hot stamping foil is generally a laminate comprised of a carrier material (often polyester or a similar material capable of release), a release film between the carrier and a subsequent decorative coat which is usually color or a metallized coat, most often aluminum or colored aluminum. The foil may contain other optional layers such as one or more protective layers, hot melt adhesive layers, etc. between the metallized layer or layers and the carrier material. More specifically, hot stamping foil can be defined as a multilayer web comprised of a backing film carrier, a release coating, one or more protective top coatings, one or more color coatings, and a hot melt adhesive in that order. The hot stamping foil is then compressed against the container with the hot melt adhesive layer being compressed against the substrate. The compress, which may be a standard hot stamping press or a hand held press, is heated to a temperature sufficient to cause the hot melt adhesive layer of the hot stamping foil to adhere to the *ink* decorated portion of the substrate. Generally this temperature ranges from about 250 to 400.degree. F. Temperatures higher than this may cause deterioration of the hot stamping foil. The application of heat causes the adhesive side of the hot stamping foil to become adhesively adhered to the *ink* design but not to the *ink*-free areas of the substrate. When the compress is removed, a portion of the foil laminate adheres to the *ink* decoration but not to the *ink* free areas of the *glass*. In particular, adhered to the *ink* design on the substrate is the hot melt adhesive layer, the color coatings, and the

protective top coatings, in that order, of the hot stamping foil. Portions of the release coating may or may not be adhered to the protective top coating because the release coating is designed to melt upon application of heat and cause the polyester carrier backing layer to release from the protective top coat layer and some remnants may remain. The resulting hot stamped substrate exhibits a metallic gold, silver, or colored appearance depending on the color of the hot stamping foil.

In yet another embodiment of the invention, it is possible to provide a decorated substrate which has a two tone effect where all or a portion of the colored **ink** on the substrate is hot stamped. In this instance a pigmented **ink** composition is applied to the substrate in a predetermined design and cured by exposing it to the radiation by which it is curable for a time sufficient to effect complete cure. Hot stamping foil is applied as described above to either the entire **ink** design or to only a part (i.e. complete or partial registration). If the hot stamping foil is applied in partial registration, or applied to a portion of the pigmented **ink** design, a pleasant two tone effect is achieved. Many times it is more economical to

print the entire design on the substrate using colored **ink** and then hot stamp over the desired portion of the design, rather than applying clear **ink** and hot stamping, and then printing colored **ink** in the desired design in a second application.

The **ink** compositions of the invention provide sufficient adhesion to **glass** as well as exhibiting sufficient resistance to scuffing and scratching to make the decorated articles suitable for use on commercial beverage and cosmetic bottles.

THE STRIPPING METHOD

The **ink** compositions of the invention can be removed from **glass** upon exposure of the **glass** to alkali. In particular, the free acid groups found in the polymerized **ink** composition are capable of reacting with the hydroxyl groups of the base to form a salt which is easily stripped or removed from the **glass**.

The aqueous alkaline solution comprises about 1-20%, preferably about 2-15%, more preferably about 2-12% by weight alkali. Suitable alkali materials include metal hydroxides (e.g. alkali metal and alkaline earth metal hydroxides) such as sodium hydroxide, potassium hydroxide, calcium hydroxide, and the like.

The cured **ink** compositions should be removed from the **glass** upon exposure to the aqueous alkali after a period of about 1 to 120, preferably about 1-60, more preferably about 1-30 minutes. The **glass** substrate is generally immersed in the aqueous alkali solution for the appropriate time period, after which the **ink** compositions are removed from the **glass** surface.

Preferably the **glass** container is subjected to the aqueous alkaline solution at a temperature of 60 to 100.degree. C., more preferably 70 to 95.degree. C., most preferably 72 to 90.degree. C.

In the most preferred embodiment of the invention the **ink** composition is removed from the **glass** containers after exposure of the **glass** to a 4% (approximately) aqueous solution of sodium hydroxide at a temperature of 70 to 100.degree. C., after 1-15 minutes.

The **decorating** method and compositions of the invention are excellent for use on **glass** containers used in the returnable beverage market. The decorative indicia applied according to the invention remains on the **glass** for the useful commercial life of the container, yet can be easily removed upon exposure to an aqueous alkali solution. This eliminates the need for paper labels and decals, which results in a significant cost savings. Also, the indicia are much more aesthetically pleasing, similar to the aesthetics achieved with ACL. Thus, beverage and cosmetic manufacturers are able to offer **glass** containers that provide aesthetics similar to ACL, with indicia that can be easily removed upon exposure to alkali solutions when the **glass** container is returned to the filler.

The invention will be further described in connection with the following examples, which are set forth for the purposes of illustration only.

EXAMPLE

A white **ink** composition was made as follows: grams wt %
 Dipentaerythritol pentaacrylate.sup.1 25.0 24.8 Epoxy acrylate +
 tripropylene glycol acrylate.sup.2 27.0 26.8 Aromatic acid methacrylate 1/2 ester 5.0 5.0 in ethoxylated
 trimethylolpropane triacrylate.sup.3 Beta carboxyethyl acrylate.sup.4 10.0 9.9 Aromatic urethane acrylate with 10.0 9.9
 polyacrylated polyol diluent.sup.5 Titaniwn dioxide (pigment) 17.0 16.9 Irgacure 1700.sup.6 3.0 3.0 Gamma-
 isocyanotopropyltriethoxysilane.sup.7 0.5 0.5 3-methacryloxypropyl trimethoxysilane8 0.5 0.5
 Trimethoxysilylpropyldiethylene triamine.sup.9 0.5 0.5 Fluorinated alkyl alkoxylate.sup.10 0.5 0.5 BYK-033.sup.11
 1.0 1.0 Modaflow.sup.12 0.8 0.8 .sup.1 SR399, Sartomer Company,
 Inc. (other polymerizable reactant) .sup.2 CN104, Sartomer Company, Inc. (other polymerizable reactant) .sup.3 SB500
 E50, Sartomer Company, Inc. (polymerizable reactant with fre acid group) .sup.4 BCEA, UCB Radcure Inc.
 (polymenzable reactant with free acid group) .sup.5 EB220, UCB Radcure Inc. (other polymerizable reactant) .sup.6
 CibaGeigy Corp. Mixture of 25% by weight bis(2,6dimethoxybenzoyl)-2,4-,4-trimethylpentyl phosphine oxide and

75% b weight 2hydroxy-2-methyl-1-phenyl-propan-1-one. (photoinitiator) .sup.7 A1310, Osi Specialities, Inc. (adhesion promoter) .sup.8 DYNASYLAN MEMO, Huls America Inc. (adhesion promoter) .sup.9 DYNASYLAN TRIAMO, Huls America Inc. (adhesion promoter) .sup.10 FC171, 3M Company (surfactant) .sup.11 BYK033, BYKChemie. A mixture of 92% by weight of petroleum distillates and 5% by weight ethoxylated alkyl phenol (defoaming agent) .sup.12 Modaflow, Monsanto, Inc. Ethyl acrylate and 2ethylhexyl acrylate copolymer (defoaming agent)

The **ink** composition was made by combining the ingredients and mixing well.

EXAMPLE

A blue **ink** composition was made as follows: grams wt %
 Dipentaerythritol pentaacrylate.sup.1 25.0 23.9 Epoxy acrylate + tripropylene glycol acrylate.sup.2 27.0 25.8 Aromatic acid methacrylate 1/2 ester 5.0 4.8 in ethoxylated trimethylolpropane triacrylate.sup.3 Beta carboxyethyl acrylate.sup.4 10.0 9.6 Aromatic urethane acrylate with 10.0 9.6 polyacrylated polyol diluent.sup.5 Ultramarine blue 5009.sup.13 20.0 19.1 Irgazin blue X-3367.sup.14 1.0 0.9 Irgacure 1700.sup.6 3.0 2.9 Gamma-isocyanotopropyltriethoxysilane.sup.7 0.5 0.5 3-methacryloxypropyl trimethoxysilane.sup.8 0.5 0.5 Trimethoxysilylpropyldiethylene triamine.sup.9 0.5 0.5 Fluorinated alkyl alkoxyate.sup.10 0.5 0.5 BYK-033.sup.11 1.0 1.0 Modaflow.sup.12 0.5 0.4 .sup.1 SR399, Sartomer Company, Inc. (other polymerizable reactant) .sup.2 CN104, Sartomer Company, Inc. (other polymerizable reactant) .sup.3 SB500 E50, Sartomer Company, Inc. (polymerizable reactant with free acid group) .sup.4 BCEA, UCB Radcure Inc. (polymerizable reactant with free acid group) .sup.5 EB220, UCB Radcure Inc. (other polymerizable reactant) .sup.6 CibaGeigy Corp. Mixture of 25% by weight bis(2,6dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide and 75% b weight 2hydroxy-2-methyl-1-phenyl-propan-1-one. (photoinitiator) .sup.7 A1310, Osi Specialities, Inc. (adhesion promoter) .sup.8 DYNASYLAN MEMO, Huls America Inc. (adhesion promoter) .sup.9 DYNASYLAN TRIAMO, Huls America Inc. (adhesion promoter) .sup.10 FC171, 3M Company (surfactant) .sup.11 BYK033, BYKChemie. A mixture of 92% by weight of petroleum distillates and 5% by weight ethoxylated alkyl phenol (defoaming agent) .sup.12 Monsanto, Inc. Ethyl acrylate and 2ethylhexyl acrylate copolymer (defoaming agent) .sup.13 Wittaker, Clark, & Daniels (pigment) .sup.14 Ciba Pigment Division

The **ink** composition was made by combining the ingredients and mixing well.

EXAMPLE

A white **ink** composition was made as follows: grams wt %
 Aromatic acid methacrylate 1/2 ester 25.0 24.5 in ethoxylated trimethylolpropane triacrylate Beta carboxyethyl acrylate.sup.2 35.0 34.2 Monofunctional acrylate resin.sup.3 15.0 14.7 Epoxy acrylate + tripropylene glycol acrylate.sup.4 5.0 4.9 Titanium dioxide 15.0 14.7 Iragacure 1700.sup.5 3.0 2.9 BYK-033.sup.6 1.0 1.0 3-methacryloxypropyl trimethoxysilane.sup.7 0.6 0.6 Gamma-isocyanotopropyltriethoxysilane.sup.8 0.6 0.6 Methyl diethanolamine 2.0 1.9 .sup.1 SB500 E50, Sartomer Company, Inc. (polymerizable reactant with free acid group) .sup.2 BCEA, UCB Radcure Inc. (polymerizable reactant with free acid group) .sup.3 Aromatic oligomer containing pendant carboxy functional groups, Henkel Corporation (polymerizable reactant with free acid group) .sup.4 CN104, Sartomer Company, Inc. (other polymerizable reactant) .sup.5 CibaGeigy Corp. Mixture of 25% by weight bis(2,6dimethoxybenzoyl)-2,4,4-trimethylpentyl phosphine oxide and 75% b weight 2hydroxy-2-methyl-1-phenyl-propan-1-one. (photoinitiator) .sup.6 BYK033, BYKChemie, A mixture of 92% by weight of petroleum distillates and 5% by weight ethoxylated alkyl phenol (defoaming agent) .sup.7 DYNASYLAN MEMO, Huls America Inc. (adhesion promoter) .sup.8 A1310, Osi Specialities, Inc. (adhesion promoter)

The ingredients were combined and mixed well.

EXAMPLE

A ultramarine blue composition was made as follows: grams wt %

Aromatic acid methacrylate 1/2 ester 25.0 24.2 in ethoxylated trimethylolpropane triacrylate.sup.1 Beta carboxyethyl acrylate.sup.2 30.0 29.1 Monofunctional acrylate resin.sup.3 15.0 14.5 Epoxy acrylate + tripropylene glycol acrylate.sup.4 5.0 4.8 Irgazin blue X-3367.sup.5 1.0 1.0 Ultramarine blue 5009.sup.6 20.0 19.4 Iragacure 1700.sup.7 3.0 2.9 BYK-033.sup.8 1.0 1.0 3-methacryloxypropyl trimethoxysilane.sup.9 0.6 0.6 Gamma-isocyanatopropyltriethoxysilane.sup.10 0.6 0.6 Methyl diethanolamine 2.0 1.9 .sup.1 SB500 E50, Sartomer Company, Inc. (polymerizable reactant with fre acid group) .sup.2 BCEA, UCB Radcure Inc. (polymenzable reactant with free acid group .sup.3 Aromatic oligomer containing pendant carboxy functional groups, Henkel Corporation (polymerizable reactant with free acid group) .sup.4 CN104, Sartomer Company, Inc. (other polymerizable reactant) .sup.5 Ciba Pigment Division .sup.6 Wittaker, Clark, & Daniels (pigment) .sup.7 CibaGeigy Corp. Mixture of 25% by weight bis(2,6dimethoxybenzoyl)-2,4-,4-trimethylpentyl phosphine oxide and 75% b weight 2hydroxy-2-methyl-1-phenyl-propan-1-one. (photoinitiator) .sup.8 BYK033, BYKChemie, A mixture of 92% by weight of petroleum distillates and 5% by weight ethoxylated alkyl phenol (defoaming agent) .sup.9 DYNASYLAN MEMO, Huls America Inc. (adhesion promoter) .sup.10 A1310, Osi Specialities, Inc. (adhesion promoter)

The ingredients were combined and mixed well.

EXAMPLE

A white *ink* composition was made as follows: grams wt %
Aromatic acid methacrylate 1/2 ester 25.0 22.8 in ethoxylated trimethylolpropane triacrylate.sup.1
Epoxy acrylate + tripropylene glycol acrylate.sup.2 10.0 9.1 Beta-carboxyethyl acrylate.sup.3 30.0 27.3 Monofunctional acrylate resin.sup.4 15.0 13.7 Polytetrafluoroethylene.sup.5 1.0 0.9 Titanium dioxide 17.0 15.5 Iragacure 1700.sup.6 3.0 2.7 BYK-033.sup.7 1.5 1.4 3-methacryloxypropyl trimethoxysilane.sup.8 0.6 0.5 Gamma-isocyanatopropyltriethylene triamine.sup.9 0.6 0.5 Monodiethanolamine 3.0 2.8 Benzophenone 3.0 2.8 .sup.1 SB500 E50, Sartomer Company, Inc. (polymerizable reactant with fre acid group) .sup.2 CN104, Sartomer Company, Inc. (other polymerizable reactant) .sup.3 BCEA, UCB Radcure Inc. (polymenzable reactant with free acid group .sup.4 Aromatic oligomer containing pendant carboxy functional groups, Henkel Corporation (polymerizable reactant with free acid group) .sup.5 SST4, Shamrock Technologies, Inc. (thickening agent) .sup.6 CibaGeigy Corp. Mixture of 25% by weight bis(2,6dimethoxybenzoyl)-2,4-,4-trimethylpentyl phosphine oxide and 75% b weight 2hydroxy-2-methyl-1-phenyl-propan-1-one. (photoinitiator) .sup.7 BYK033, BYKChemie, A mixture of 92% by weight of petroleum distillates and 5% by weight ethoxylated alkyl phenol (defoaming agent) .sup.8 DYNASYLAN MEMO, Huls America Inc. (adhesion promoter) .sup.9 A1310, Osi Specialities, Inc. (adhesion promoter)

The composition was made by combining the ingredients and mixing the ingredients well.

EXAMPLE

A blue *ink* composition was made according to the following formula:
grams wt %
Aromatic acid methacrylate 1/2 ester 25.0 24.7 in ethoxylated trimethylolpropane triacrylate.sup.1 Epoxy acrylate + tripropylene glycol acrylate.sup.2 10.0 9.9 Beta-carboxyethyl acrylate.sup.3 25.0 24.7 Monofunctional acrylate resin.sup. 15.0 14.8 Ultramarine blue 5009.sup.5 15.0 14.8 Irgazin blue X-3367.sup.6 1.5 1.5 Polytetrafluoroethylene.sup.7 1.0 1.0 Iragacure 1700.sup.8 3.0 3.0 Benzophenone 3.0 3.0 BYK-033.sup.9 1.5 1.4 3-methacryloxypropyl trimethoxysilane.sup.10 0.6 0.5 Gamma-isocyanatopropyltriethoxysilane.sup.11 0.6 0.5 .sup.1 SB500 E50, Sartomer Company, Inc. (polymerizable reactant with fre acid group) .sup.2 CN104, Sartomer Company, Inc. (other polymerizable reactant) .sup.3 BCEA, UCB Radcure Inc. (polymenzable reactant with free acid group .sup.4 Aromatic oligomer containing pendant carboxy functional groups, Henkel Corporation (polymerizable reactant with free acid group) .sup.5 Wittaker, Clark, & Daniels (pigment) .sup.6 Ciba Pigment Division .sup.8 CibaGeigy Corp. Mixture of 25% by weight bis(2,6dimethoxybenzoyl)-2,4-,4-trimethylpentyl phosphine oxide and 75% b weight 2hydroxy-2-methyl-1-phenyl-propan-1-one. (photoinitiator) .sup.9 BYK033, BYKChemie. A mixture of 92% by weight of

EXAMPLE 7

EXAMPLE 8

While the invention has been described in connection with the preferred embodiment, it is not intended to limit the scope of the invention to the particular form set forth but, on the contrary, it is intended to cover such alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims.

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